DETERMINATION OF ARSENIC AND SELENIUM IN SEDIMENTS BY HYDRIDE EVOLUTION

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The Honourable
Harry C. Parrott, D.D.S.,
Minister

K.H. Sharpe,
Deputy Minister

DETERMINATION OF ARSENIC AND SELENIUM IN SEDIMENTS BY HYDRIDE EVOLUTION

by

F.C. DARCEL, D. CHAN, L. DOEHLER & P. O'DELL
Ontario Ministry of the Environment
Laboratory Services Branch

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ABSTRACT

Determination of Arsenic and Selenium in Sediments by Hydride Evolution

F. C. Darcel, D. Chan, L. Doehler & P. O'Dell
MOE Laboratory Services Branch, Toronto

Automated procedures for arsenic and selenium analysis in sediments used in the OMOE Sediment and Soils Laboratory are described. Heavy metal interferants are removed by adsorption on resin (Chelex 100) prior to hydride evolution in the selenium procedure. The methods can also be used for soils and industrial wastes.

Some of the data obtained for near-shore Great Lakes sediments and land drainage areas is reviewed.

The procedure for selenium is promising, but problems still exist at high interferant levels indicating the need for further study.

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APPENDICES (cont'd)

THE DETERMINATION OF ARSENIC AND SELENIUM IN SEDIMENTS BY HYDRIDE EVOLUTION

Arsenic and selenium both have environmental significance. Arsenic is toxic, may be carcinogenic, and is of no use in the body. Selenium, on the other hand, is an essential nutrient with a narrow range between deficiency and toxic excess. Low concentrations are toxic to creek chubs and zebra fish. Under some conditions, selenium may help to counter the toxicity of cadmium and mercury. Both arsenic and selenium can be methylated by micro-organisms.

Arsenic and selenium both occur in higher concentrations in sediments than in the overlying waters adsorbed and desorbed from sediment acting as a "sink" (Darcel, 1975).

Arsenic can be "fixed" in soil (and sediment) by mechanisms similar to those for phosphate, viz the sesqui-oxides (Fe, Mn), free iron oxide, calcium and lead (Hess & Blarschar, 1976). Clay also plays an important role (Johnson & Hiltbold, 1969; Helmke et al, 1977). Of interest is the low solubility of calcium arsenate and even more so ferric arsenate (K_{sp} 6.8×10^{-19} and 5.7×10^{-21}, respectively). Arsenic can be brought into solution by low Eh and pH conditions (D. & Swaboda, 1972) and phosphate. Similar extractants can be used for "available" or "extractable" arsenic as for phosphate (e.g. 0.05 N HCl/.025 N H_2SO_4, 0.5 N NH_4F, 0.5 N H_2SO_4, 0.1 N Na OH). 1 N NH_4Cl may be most suitable for water-extractable As (Woolson, 1971).

Selenium is also "fixed" by sesqui-oxides and iron (Moxon, 1976) and by kaolinite and other clays (Jacobs et al, 1970), organic matter and micro-organisms. It is leached principally as selenite (Gissel-Nielson, 1976) and can also be displaced by phosphate (Rajan & Watkinson, 1976). The most useful extractant appears to be boiling water (Olsen et al, 1942). 1 M HNO_3 and 0.1 M citric acid have been used for both selenium and arsenic.

Determinations of total arsenic and selenium are important as indicators of potential problems and in studies of mass movement. Hot acid extraction has been used at the Ontario Ministry of the Environment (OMOE) although it is recognized that highly insoluble forms may not have been dissolved. Arsenic occurs in highly variable concentrations in sediments and soils in Ontario. (OMOE data in Table I). High concentrations in the percent range are found in some mine wastes. Much less data is available for selenium with values generally an order of magnitude lower (Table I). The mean value for arsenic in Lake Huron is given as 1.09 ug/g (p.p.m.) and for Georgian Bay and the North Channel of Lake Superior as 4.16 ug/g (International Joint Commission, 1977). In a study of Ontario Watersheds draining into the Great Lakes (O'Neill, 1978) suspended sediment and bed material were analyzed for arsenic. The highest values reported were 19 ug/g and 10 ug/g As, respectively, for suspended sediment and bed material. (Table II)

ANALYTICAL METHODS

A wide range of methods are available for the determination of arsenic and selenium in sediments. Some methods such as neutron activation analysis, X-ray fluorescence and powder spectrograph do not require prior solution of the sample and hence measure total As or Se. Alkaline fusion methods as used for arsenic (Smith et al, 1977) can also be considered to measure total constituent. Most hot acid dissolution procedures do not bring all the sample into solution as some "residuals" (principally silicates and silica) may remain undissolved unless HF is used. With most procedures, however, some As III may be volatilized as As F_3 and a preferred route appears to be pre-treatment with $HNO_3/HClO_4$ (Bojo, 1978). Hot acid digestions with HCl/HNO_3, H_2SO_4/HNO_3 or $HClO_4/HNO_3$ have

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been most commonly practiced. HNO_3 alone has also been used and, for arsenic, cold 9.6 N HCl (Forehand et al, 1976). Vapour phase HF/HNO_3 treatment is an interesting development (Feldman, 1977).

Following dissolution, various finishes can be used, such as the widely used colorimetric and fluorimetric procedures for As and Se, respectively (silverdiethyl dithio carbamate for As and 2.4 diaminonapthalene for Se). Electrochemical procedures (differential pulse) and gas chromatography show great promise, principally because of high sensitivity. Atomic absorption spectrophotometry (AAS) has become increasingly popular by flame, flameless and hydride reduction procedures. Multi-element analysis of hydrides by inductively coupled plasma holds promise.

HYDRIDE METHOD

The hydride reduction tube furnace AAS method was selected at the OMOE Central Laboratories for the determination of As and Se because of its good detection limits, high specificity, isolation from some interferants and ease of automation. Drawbacks are the relatively narrow operating range often necessitating dilutions and the presence of interferants in the hydride evolution step, particularly for selenium.

The principal of the hydride reduction method is to first digest the sample under conditions that will bring the As or Se into solution and to convert them to the optimum valence state (As_{III} and Se_{IV}) followed by reduction to the hydride (AsH_3 and H_2Se), inert gas displacement and burning of the hydride in the optical path of an atomic absorption spectrophotometer.

Production of the optimum valence state normally requires a reduction step following acid dissolution. Under

the conditions of $HNO_3/HClO_4/HF$ digestion As was in the form of As_V whereas Se varied in oxidation state (Bojo, 1978). Hot concentrated HCl reduced Se_{VI} to Se_{IV} although prolonged reduction has to be avoided because of the formation of volatile Se OCl_2 Se O_2 2HCl (Shimoishi, 1976). HCl has also been used as a reductant for As_V to As_{III}; in some procedures iodide is added as a pre-reductant.

Sodium borohydride is now commonly used as a reductant because of its convenience; earlier systems used zinc or aluminum metal slurries.

In the OMOE Sediment and Soils Laboratory, overnight HCl/HNO_3 digestion followed by hot HCl has been used routinely for As (the same digestate as for metal extraction). An HNO_3/H_2SO_4 digestion is used for selenium. A good correlation was found for As following HCl/HNO_3, HNO_3/H_2SO_4 and extraction with hot dilute HCl (Darcel, 1977). Other laboratories within the Ministry use $HNO_3/HClO_4$ (Vijan & Wood, 1975).

Manual and continuous flow systems can be used following the digestion step. In manual systems, such as those described by Thompson and Thoresly (1977) and McDaniel et al (1976) and several commercially available units generators are used for batchwise production of hydride. Reservoirs (Schmidt & Royer, 1973) and cold traps can be used to concentrate the hydride for greater sensitivity. Syringes can be used as generators to mix the sample with reagents, but also as a means of injecting the head gas (hydrides) into an inert gas stream flowing through the furnace (Van Loon & Brooker, 1974; Smith et al, 1977).

Continuous flow systems permit automated analysis (Vijan & Wood, 1975; Pierce et al, 1976, 1977). The procedure used by the OMOE Sediment & Soils Laboratory is based

on that of Vijan and Wood. The hydride evolved by mixing a stream of acidified sample with borohydride in a mixing coil is swept by inert gas through a gas-liquid separator. The gas phase enters at the mid-point of an open ended electrically heated quartz tube.

The atomic absorption of the hydride burning in hydrogen generated by the borohydride is measured using either hollow cathode lamps or electrodeless discharge lamps as sources. Concentrations are determined from peak height measurements on a strip chart.

Several factors affect the sensitivity of the test, such as sample size, borohydride concentration, inert gas flow and if argon or nitrogen, quartz cell size and temperature and source - hollow cathode or electrodeless discharge. Interference in the hydride evolution step can also play a major role in sensitivity and reproducibility, particularly for selenium. Improper digestions, with incomplete conversion to As_{III} or Se_{IV} or residual nitric acid suppress peak height measurements.

The composition of the sample digestate tube can also affect the results. Pierce et al (1976) found up to 73 per cent analytical suppression for arsenic with polyethylene and 82 per cent for selenium. There was no suppression with Pyrex glass, but intermediate amounts with polystyrene. Shendrikar and West (1974) made similar observation. Pyrex is, therefore, the preferred material of construction.

INTERFERENCES

Interference in hydride evolution have been extensively studied (Pierce et al, 1976 and 1977; McDaniel et al, 1976). Competition for the available reducing agent is

an important factor. Some workers (Vijan & Wood, 1975) and the present study have found copper to be most serious. Pierce et al (1977) noted suppression of As and Se by Cr_2O_7, MnO_4, VO_3, S_2O_8 and MoO_4, HNO_3 and H_2SO_4. If the borohydride is added before HCl suppression of signal can be serious.

Contact time is important. Pierce et al (1977) used a 40 foot delay coil.

Incomplete separation of the hydride gas from the aqueous phase can also lead to poor recoveries, particularly for selenium because of the higher solubility of the hydride in water. Pierce and associates (1977) used a Goulden stripping column and condensing column (Goulden and Brooksbank, 1974) in place of a simple gas-liquid separator. It is of interest to note that Pierce found fewer interferences by the continuous flow method than by manual or flameless methods.

Drying of the gas stream going to the furnace is important. Vijan and Wood used concentrated sulphuric acid; other workers have found calcium chloride more efficient (McDaniel et al, 1976).

A problem noted at OMOE for selenium has been "memory effects" in which interferants in a sample can affect later samples and standards. Absorption on surfaces can also be a problem, but can be circumvented by running a high concentation initially and repeating standards until peak heights have stabilized.

Standard practice in the Sediment & Soils Laboratory has been to analyze samples using 0.5 g and 1.00 g portions and adjusting the digestates to the same volume (50 mls) as a quick check for interferants - the concentration in solution for the 1.00 g portion should be 2X that of the 0.5 g. In most instances, agreement was satisfactory for arsenic. Where

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there were indications of interferances it was usually possible to dilute them out because of the relatively high arsenic content in relation to the detection limit. The method has been standardized and some quality control data is given below.

DETERMINATION OF ARSENIC

In the digestion procedure samples are heated overnight with HCl/HNO_3 on a hot plate set at low temperature. All samples evaporate to dryness during this step and are then taken up in 5 ml HCl and 5 ml water and heated to just below the boil prior to filtering and making up to volume. In most instances, an aliquot has to be taken and diluted because of the high sensitivity of the hydride method.

The diluted aliquot is placed in a Pyrex tube of a Gilson sampler and coupled to a Technicon pump. Sulphuric acid and fresh borohydride are added. Arsine gas is sparged out with nitrogen, separated from the liquid phase, dried over sulphuric acid and passed to the quartz cell. The absorbance is read at 193.7 nm on a Varian AA-4 using an electrodeless discharge lamp. Using the 2 mv scale of a recorder the detection limit is 3 ppb in solution with 250 ppb full scale. For an undiluted digestate of a 0.5 g sample the above specifications represent 0.3 ug/g (ppm) and 25 ug/g, respectively, in the original sample. (100 X dilution). The values for the 1.0 g portion are 0.15 and 12.5 ug/g (50 X). Blanks are not usually a problem. The flow diagram is given in Figure I.

QUALITY CONTROL FOR ARSENIC

Routine data generated for arsenic from 0.50 and 1.00g was used for estimated within-run precision. Between run

variability was obtained from the data for in-house reference samples included in the digestion and analysis steps in each run. Blanks were also included to correspond with the acid addition rates for 0.50 and 1.00 g portions. (Table III, Fig. II & III)

The A and B control chart method based on Youden plots as applied by D. E. King of the OMOE Quality Assurance Office was used for the reference samples, treating the 0.50 g and 1.00 g results as for separate samples. (Figures IV & V)

The necessity for good spectrophotometer operation was very evident from the A and B plots for 1976 and to September 1977. Towards the end of this period, operation was switched from an early model Hilger & Watts Atomspec to a Varian AA-5. The latter was much noisier resulting in what appeared to be out-of-control operation, particularly apparent in the A vs B plot for Reference 14 (Trent Canal, subsurface). More recently, satisfactory control resulted from the use of a Varian AA-4 with an electrodeless discharge lamp. (Figure IVB)

Variability was higher for Reference 15 (Trent Canal - surface) possibly because of problems with digestion due to the higher organic matter content.

DETERMINATION OF SELENIUM

With selenium, concentrations in most sediments are an order of magnitude lower than those for arsenic hence interferants, apart from being more severe, cannot be diluted out. There was also considerable divergence in opinion in the literature as to which metals were the most serious interferants. It was decided, therefore, to remove most heavy metals by resin treatment. Vijan and Wood had attempted to use resin for vegetation samples high in metals, but rejected it as impracticable, preferring the method of standard

additions. Chelex 100 was selected for the present study because of its high adsorption potential for metals such as copper, purity and availability in fine mesh sizes.

ION EXCHANGE METAL INTERFERANT REMOVAL

Experimentation with in-line Chelex 100 resin columns was unsuccessful because the columns rapidly fouled with increase in pressure drop and reduction in flow. In addition, the resin was not operating at its optimum pH (pH > 6) for ion exchange in acid digestates (pH < 1). It was decided, therefore, to slurry the resin in a buffer* and mix it with an aliquot of the sample such that the final pH was ≃ 6. A continuous filtration assembly using a paper tape filter was devised to remove the resin prior to the addition of acid. The buffer medium selected was sodium acetate/sodium hydroxide.

In the original arrangement the resin slurry was continuously stirred in a beaker with a magnetic stirrer. The slurry feed was pumped through a flow tube using a Technicon pump. There were frequent stoppages due to flow tube rupture because of non-uniform slurry solids content and resin clumping using this method for resin feed and suspending the resin. Greatly improved performance resulted by using a finer mesh size of Chelex 100 (200-400 mesh instead of 100 - 200) and by maintaining a high velocity, high flow rate recycle stream of resin slurry using a separatory funnel as reservoir and a separate high capacity peristaltic pump. The resin slurry feed line to the Technicon pump was as short as practicable, bleeding off from a loop in the recycle line. There were some mechanical problems due to paper tape failure, but these were largely overcome by minor modifications in design of the filtration assembly and close attention to guiding. A "wash-

*sodium acetate/sodium hydroxide

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off" unit using service water was provided to remove the resin from the continuous tape filter. Resin was collected in a settling tank to permit recovery, regeneration and reuse.

Control of pH in the diluted digestate was important. If the pH was too high ferric hydroxide precipitated out, masking the resin and possibly co-precipitating the selenium. If the pH was too low the resin was inefficient, as discussed earlier.

To permit a relatively constant sample acidity the digestion procedure was modified as initial attempts with HCl/HNO_3 as used for arsenic gave low recoveries. Poor recoveries were also obtained for $HClO_4/HNO_3$ in a limited study.

Digestions were conducted at low temperature overnight using air condenser with a constant volume of sulphuric acid (2 mls), varying the amount of nitric acid with sample size and organic matter content. The nitric acid was volatilized overnight leaving the acidity due to the sulphuric acid. (Doehler, 1976).

For some samples higher yields of selenium were obtained compared with those for no resin treatment. For others, however, there was a reduced yield using the 1.00 g sample weight compared with 0.5 g, poor spike recoveries, and memory effects on following samples and standards suppressing peak heights and shifting baselines.

There was some improvement by including an in-line heater (87.5°C) and condenser after the borohydride mixing coil to speed up the reaction and decrease the solubility of H_2Se, respectively and by increasing the contact time with resin by incorporating a 40 ft. coil.

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It was felt, however, that some of the inefficiency of the resin was due to the high concentration of iron in most sediment digestates competing with the more sensitive metals (e.g. Cu, Ni) for the available resin adsorption sites. Uchida et al (1977) had found that malonic acid was the most effective complexing agent for iron, permitting Chelex 100 in ammonium form to remove Cu, Ni, etc. from solution at pH6 isolated from iron, prior to AAS analysis.

Malonic acid - ammonia was investigated, therefore, as an alternative to sodium acetate - sodium hydroxide. An excess of ammonia above that required stoichometrically to form ammonium malonate, was required to adjust to pH. Appreciable improvement was noted in selenium recovery in solutions with interfering metals (Table IV) and difficult samples. The use of the 40 ft. coil was inconvenient, however, because of the additional 15 minutes delay at start-up and shut-down. Heating the resin slurry - sample in an in-line heating bath reduced the residence time in the system while permitting effective exchange with the resin for most samples. A minor modification also introduced was to include a second sulphuric acid water vapour trap ahead of the quartz tube. The use of an electrodeless discharge lamp gave some improvement.

Greater sensitivity was attained by the use of a smaller diameter quartz tube (0.5 cm approx.) as used for water analysis and lowering the furnace temperature (Variac setting). The proportion of resin slurry to sample was increased (by changing flow tubes). The decrease in sensitivity with smaller sample size was compensated for by the increase due to the furnace modifications noted above. No change was made in the inert gas supply. Nitrogen was used in preference to argon (as used in water analysis for As and Se)because

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of its lower cost.

Visually, the effect of the malonate-ammonia system could be seen in that the resin beads were no longer stained with iron and there were no further problems of precipitation of ferric hydroxide.

Some samples were run comparing 0.25 g with 0.50 g with higher recoveries for the former. Very limited work with the Technicon hot block using 0.25 g samples under digestion conditions used for mercury at OMOE gave promising results possibly because the higher temperature (200^{o}C) in the heating cycle resulted in more complete removal of nitric acid.

Details of the most recent system are appended. The equipment is conveniently mounted on a laboratory trolley and can be quickly attached to the quartz cell and atomic absorption spectrophotometer used for arsenic or selenium in waters.

Because of the changes in process for selenium, little statistical data is available to date.

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DISCUSSION

1) Arsenic

Using the procedures described, few sediment or soil samples analyzed for arsenic in the Sediment and Soils Laboratory since 1975 have given indications of interferences. In most cases where interferences were suspected, dilution with distilled water was adequate. Use of HCl/HNO_3 digestion may yield slightly lower values for As than H_2SO_4/HNO_3 but, in most cases, the convenience and time and cost saving of using the same digestate as for metals and the reproducibility of the data outweighs the possibility of slightly lower results. With the flow arrangement used, operation can be easily and rapidly converted from the system used for the analysis of waters (in the ppb range) to that used for digested solid samples.

Care must be taken in the operating condition of the AAS used, e.g. good peaks were obtained for a Varian AA-4, but very noisy output on one of the AA-5 instruments. In contrast, satisfactory performance has been obtained by Vijan using an AA-5.

The system normally runs with a minimum of attention. The most time consuming element is the dilution of samples which run As-Is could be off-scale.

It is of interest to note that good agreement was obtained between the analysis of arsenic by the routine HCl/HNO_3 and hot HCl extraction (Darcel, 1977). On the other hand, there was little success in attempting to couple the hydride evolution procedure to the alkali fusion method for total As of Smith et al (1977) or to multi-acid digestion, including HF, recommended for "total" metals by the Soil

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Research Institute, Ottawa. (The latter problem was possibly due to AsF_3 volatilization discussed earlier).

It is felt, however, that the procedure used does provide a measure of the potential environmentally significant fraction of the total arsenic. Limited data has been obtained to date by this Laboratory of readily releaseable arsenic using milder extractants such as those already discussed, but this situation will hopefully be remedied.

There is still room for improvement in reducing between run variability and systematic errors. The higher variability for a highly organic sample such as Reference 15, indicates that there may be a need for evaluating a modified digestion procedure for such samples.

2) Selenium

The resin-malonate pre-treatment removed metallic interference to a degree, but care is needed in limiting sample size and checking spike recoveries when interferences are suspect. Limiting sample size, on the other hand, leads to poorer detection limits; however, for most data users, detection limits are still adequate. Errors are introduced because of base-line instability and memory effects on following samples and standards.

Recent literature indicates that it may be possible to reduce interference problems by providing optimum conditions for hydride evolution, such as the use of delay coils and stripping and cooling columns. More study is required in this area.

In spite of the problems, the resin-pre-treatment has proved successful in many instances. The use of the Technicon

hot block and the digestion procedure used for mercury (with smaller sample size - 0.25 g) appeared promising.

For some samples, the hydride method may be unsuitable because of interferences and it may be necessary to use a gas chromatographic method such as that developed at the Ministry of the Environment (B. Neary) or Young (1973).

Good agreement was obtained with the recommended value for selenium in standard fly ash, even prior to the use of malonate (10.3 & 11.1 ppm vs certified value of 9.4 $\pm$ .5).

Values for total selenium and arsenic in a Canada Certified Reference Materials Project soil (SO-4) have been recently established by neutron activation analysis at the University of Wisconsin (Koons & Helmke,* 1978) and it will be of interest to compare results by hydride evolution. Unfortunately, however, problems have been experienced in attempting to determine either arsenic or selenium after the dissolution either by alkali fusion or mixed acid digestion (including HF) due to blank problems and poor recoveries, indicating the need for further study.

Figures IX, X and XI are of interest. Good calibration curves can be obtained routinely for aqueous standards, digested and undigested, linear to at least 80 ppb in solution (Fig. IX). Following nitric-sulphuric digestion with resin treatment some samples such as S50.2-1 demonstrate 100% recovery of 40 ppb spike (S^+ in Fig. X) whereas for other samples recovery is only 50-70%. However, without resin treatment (e.g. S9-11 in Fig. XI) the peak height indicates a much lower concentration of selenium and there is low spike recovery (4% vs 56%).

*Koons, R.D. and P.A. Helmke, 1978. Neutron activation analysis of standard soils. Soil Sci. Soc. Amer. J. 42:237-240.

CONCLUSIONS

1. The aqua-regia digestion automated hydride evolution method for arsenic is practicable for sediments and provides a useful measure of the acid soluble fraction.

2. The sulphuric-nitric acid digested, malonate-resin pre-treated, hydride method for selenium is also satisfactory for most samples provided steps are taken to test frequently for interferances, i.e. smaller sample size digestate, dilutions and spike recovery studies.

3. Other procedures such as the manual injection hydride method, gas chromatograph analysis, neutron activation analysis or X-ray fluorescence may be preferable for difficult samples.

RECOMMENDATIONS

A. Arsenic

1. The procedure described can be used to measure acid-soluble arsenic.

2. More work is required in the application of the hydride technique to the determination of true total arsenic following dissolution in alkali or mixed acids (HNO_3/$HClO_4$/HF). In the latter, pre-treatment with HNO_3/$HClO_4$ (Bojo, 1978) should be evaluated as a route to prevent volatilization of AsF_3.

3. More comparisons should be made with emission spectrograph-inductively coupled plasma (ES-ICP), powder spectrograph and XRF data with a view to replacing the hydride method because of their potentially lower cost and increased speed.

4. Samples should be run in duplicate, preferably 0.5 g and 1.0 g. Where there is poor agreement between duplicates

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the presence of interferants should be checked by dilution, spiking and resin treatment (as for selenium).

5. Consideration should be given to modifying the hydride procedure with a view to standardizing flow conditions for As and Se in sediments (and soils).

6. More emphasis should be placed on the determination of "extractable" arsenic using weak acid or organic extractants and in assessing its environmental significance.

7. The practice of analyzing two in-house reference standards in each digestion run should be continued and supplemented by the analysis of certified standards to permit quality control.

8. The A and B quality control charts should be reviewed more frequently and immediate action taken to minimize systematic error, e.g. check on digestion conditions, standards and calibration errors, and instrument operation.

B. Selenium

Similar recommendations to those for arsenic are applicable to an even higher degree to the determination of selenium. Other recommendations are as follows:

1. Smaller sample sizes should be investigated (0.1 g and 0.2 g) to reduce interferances.

2. Further study should be made of the applicability of the hot block digestion procedure for mercury used at OMOE.

3. Resin pre-treatment and hydride evolution conditions should be "tuned" for maximum recovery of selenium.

4. Further investigation should be made of the use of hot water and other extractants as routes to measuring the

environmentally significant fraction of selenium.

5. Consideration should be given to coupling hydride evolution with malonate-resin pre-treatment to a double beam AAS or ES-ICP to permit multiple metal analysis by the hydride method. A modification of the manual syringe injection procedure (Van Loon and Brooker, 1974; Smith et al, 1977) should be evaluated first as it can be more readily coupled to ICP and dedicated computer operation.

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APPENDIX I

ARSENIC

RANGES IN CONCENTRATION OF ARSENIC AND SELENIUM

ARSENIC IN SEDIMENTS IN THE URBAN LAND USE STUDY (PLUARG)

DETERMINATION OF ARSENIC IN SEDIMENTS - AUTOMATED HYDRIDE METHOD

TABLE I

ARSENIC & SELENIUM IN ONTARIO

EXAMPLES OF RANGES IN CONCENTRATION*

	ARSENIC ug/g	SELENIUM ug/g
SOILS		
Sludge Disposal Fields Peterborough	0.6 - 9.5	<.03 - .88
Newmarket	1.2 - 1.8	.06 - .7
Nipissing	1.2 - 1.7	<.1 - .2
North Bay	.4 - 1.8	.15 - .37
SEDIMENTS		
Speed River	.7 - 1	.07 - .56
Dunnville Reservoir	1.5 - 6.4	
Grand River - Suspended Sediments	3.7 - 6.5	0.5 - 1
Hamilton Harbour	5.7 - 15	
Moira Lake	15 - 1000	
Jackfish Lake	1.6 - 7.4	
Wabigood	.5 - 5.0	
English	.28 - 13	
Farr Creek	25 - 880	
Lake Timiskaming		
MINE WASTE		
Cobalt	54,000	
Balmertown gold mine	1,600	
OTHER MATERIALS		
Digested Sludge - Chatham	19	

* Samples analyzed by OMOE - Sediment & Soils Laboratory

TABLE II

ARSENIC IN SEDIMENTS

URBAN LAND USE STUDY PLUARG*

Ontario Watersheds Draining Into Great Lakes

	Arsenic ug/g			
	N	MIN	MAX	
Suspended Sediment	103	1.1	19	Schneider Cr.
Bed Material	116	.06	10	Essex, St. Clair R.

Schneider Cr. - Loading**

	Per cent
Dissolved	80
Suspended	20
Bed	<1

**Peak Loads March - April
August - September

*J.E. O'Neill, 1978. Urban Land Use Technical Report. (Canadian). Int. Joint Comm. - Pollution from Land Use Reference Group. (To be published).

DETERMINATION OF ARSENIC IN SEDIMENTS - AUTOMATED HYDRIDE METHOD

DIGESTION - Aqua Regia

1. Add 5 ml. concentrated nitric acid and 10 ml. concentrated hydrochloric acid to 0.50 g. oven or air-dried sample, pulverized and sieved to <16 mesh, contained in 125 ml. Phillips beaker. Use twice the quantity of acid for 1.00 g. portion of sample.
2. After 30 minutes or when effervescence has ceased, place on hot plate with temperature control and turn ON to low heat (approx. 80°C).
3. Heat overnight (about 16 hours) by which time digestates will have evaporated to dryness.
4. Cool, add 5 ml. concentrated hydrochloric acid and wash down sides of beaker with 5 to 10 ml. distilled water. Warm for 15 minutes.
5. Filter through fine filter paper (such as Schleicher and Schuell No. 589), wash with distilled water into 50 ml. graduated tube, make up to mark and shake to mix.

ANALYSIS

1. Assemble autoanalyzer system as shown in Figure I. System is connected by Tygon tubing to the mid-point of an open-ended 0.5 cm. I.D. x 10 cm. electrically heated quartz tube in the optical path of a single beam atomic absorption spectrophotometer.

   Operating conditions with the Varian AA-4 are as follows:

Wavelength	- 193.7 nm
Slit	- 300 nm
Current	- AA-4 source 2mA: EDL power source 10 watts
Mode	- Absorbance
Damping	- D (max.)
Scale	- No expansion

Tube heater (Variac) - 10 (140V)
Recorder
Speed - 20 cm/hr
Sensitivity - 2 mV span
Full Scale - 250 ppb As
Detection - 3 ppb As

2. Make up fresh 1 per cent sodium borohydride and set up reagent flows as indicated in Figure I. Place about 10 ml. digested and undigested arsenic standards to 250 ppb (from 1000 ppm As stock made up from arsenic trioxide in dilute nitric acid), digested blanks and digested sample aliquots in Pyrex glass tubes in sampler tray.

3. Start up auto-analyzer, quartz tube, atomic absorption spectrophotometer and recorder and adjust nitrogen gas flow and instrument conditions as required for minimum noise and maximum sensitivity.

4. Place blanks and standards at intervals in the auto-analyzer sampler sequence to check for changes in sensitivity. Also include two digested in-house reference samples to check on between run variability.

5. Prepare calibration curve using Hewlett-Packard M9830 mini-computer (or equivalent) and calculate concentrations of arsenic in sample digestates from peak heights, allowing for blanks. (Figures II and III). Check that concentrations in solution of 1.00 g. sample digestate are approximately 2x that of 0.50 g. sample aliquot. If not, digestion may have to be repeated or different size aliquot taken.

6. Calculate concentration in original sample by multiplying concentration in solution by 50x or 100x dilution factor.

7. Check that concentrations for in-house reference samples

are within control limits established by A vs B procedure for each reference (1.00 v 0.50 g.). If not, check standards or for other problems. Review control limits periodically. Check agreement between sample duplicates and repeat if difference is greater than that expected by the within-run precision as indicated by Table III.

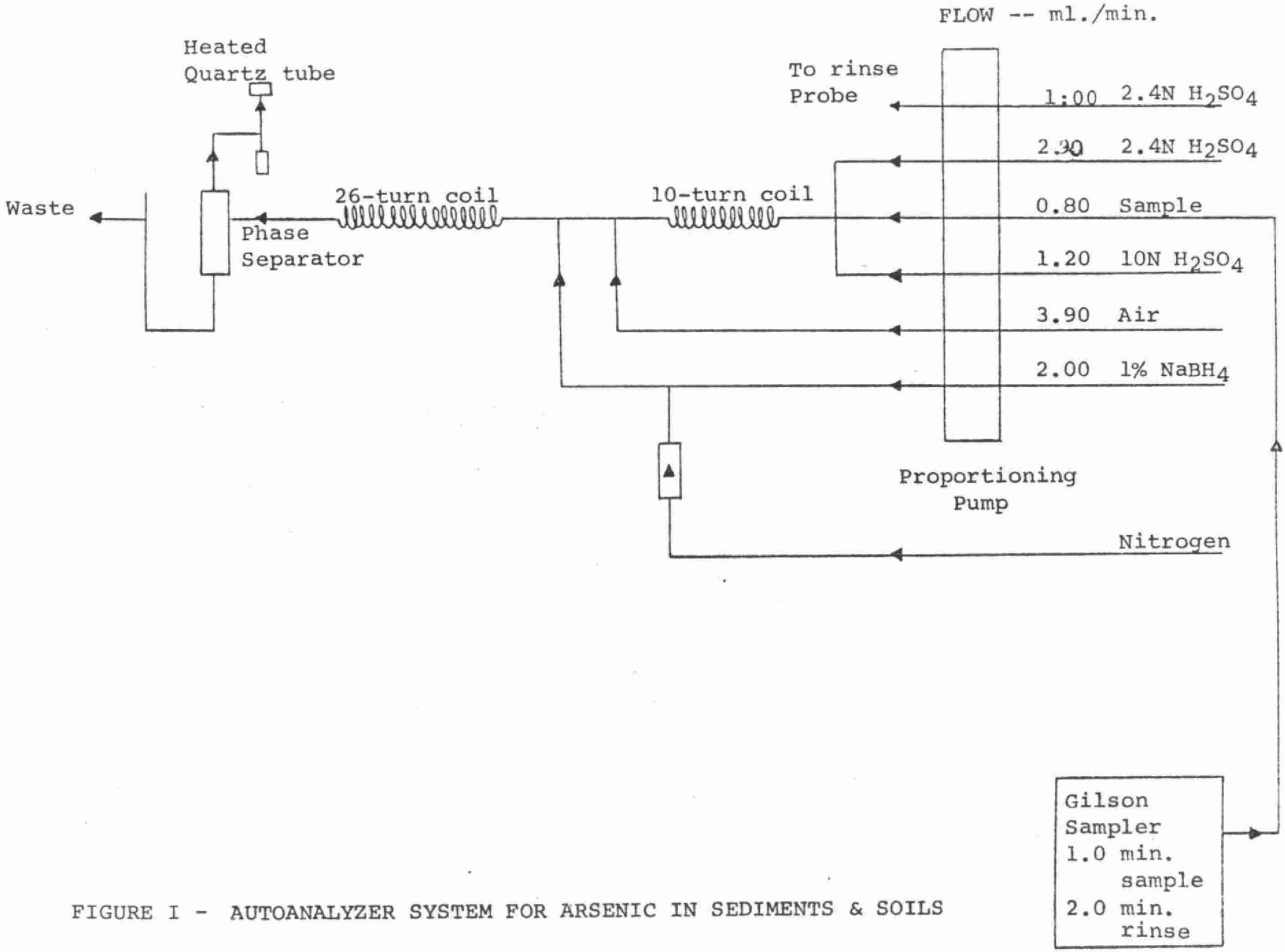
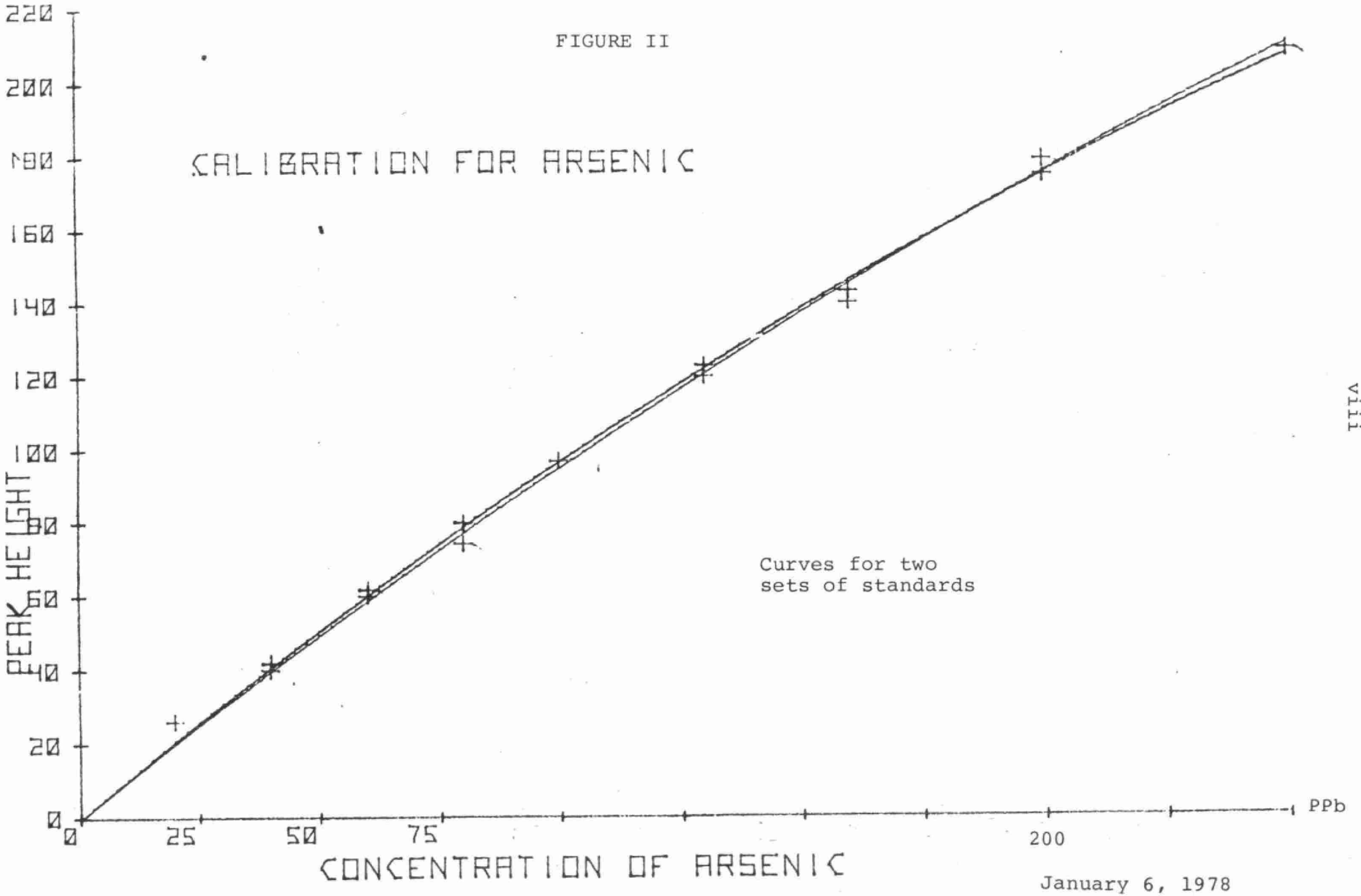


FIGURE I - AUTOANALYZER SYSTEM FOR ARSENIC IN SEDIMENTS & SOILS

FIGURE II



January 6, 1978

FIGURE III - ARSENIC

$HCl-HNO_3$ DIGESTION

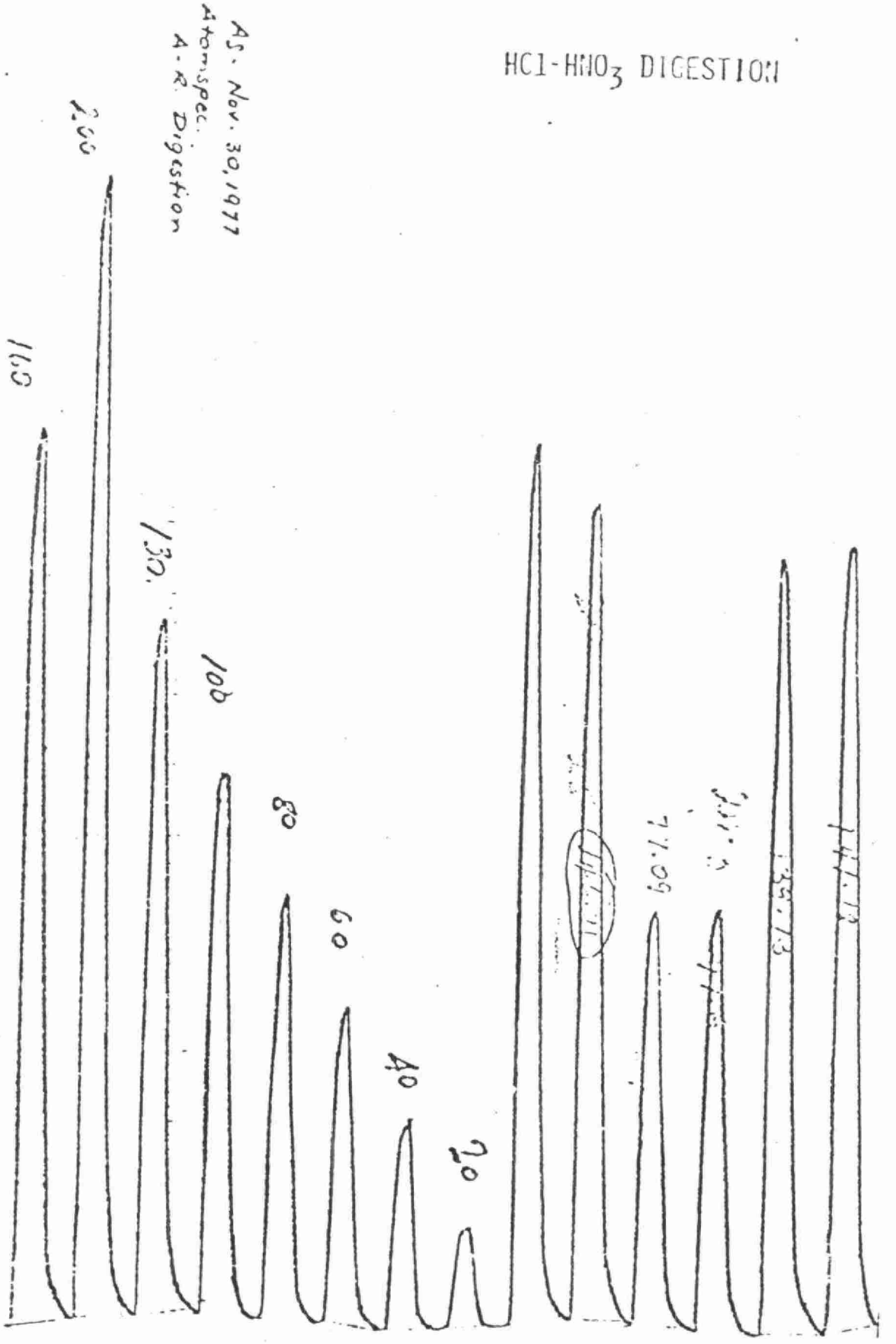


TABLE III

ARSENIC

Precision Data* - Soils & Sediments

Within-Run Precision

CONCENTRATION	WITHIN-RUN STD. DEV.	RELATIVE STD. DEV.	NO. OF DUPLICATES
ug/g	ug/g	%	
0 - 5	.24	9.5	75
5 - 10	.49	6.5	25
10 - 50	2.2	7.5	30
50 - 100	5.7	7.6	90
100 - 300	9.9	5.6	36

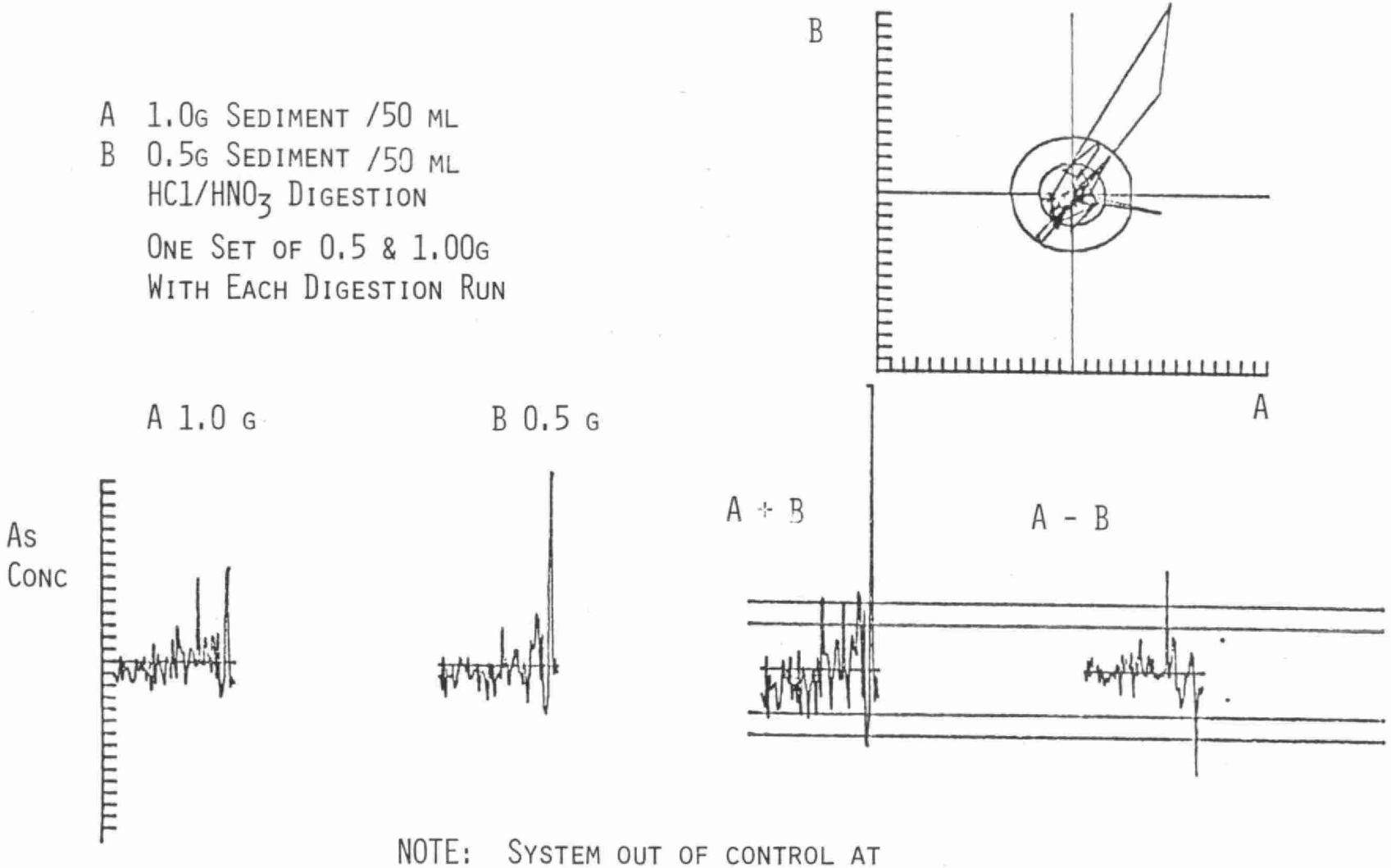
BETWEEN RUN PRECISION

	MEAN CONC. ug/g		BETWEEN RUN STD. DEV. ug/g	NO. OF DUPLICATES
Ref. 14	1.00g	2.41	.211	25
	0.50g	2.41	.218	16
Ref. 15	1.00g	2.98	.254	17
	0.50g	3.15	.285	15

*Based on routine data with HCl/HNO_3 digestion. July - September 1977. Memo P. Fellin, Oct. 1977.

FIGURE IVA - ARSENIC IN REFERENCE 14
1976 & 1977 DATA (TO SEFT)

A 1.0G SEDIMENT /50 ML
B 0.5G SEDIMENT /50 ML
HCl/HNO_3 DIGESTION
ONE SET OF 0.5 & 1.00G
WITH EACH DIGESTION RUN



NOTE: SYSTEM OUT OF CONTROL AT
END OF RUN DUE TO NOISY AAS

Ministry of the Environment
Ontario

FIGURE IVB

A vs. B DATA REPORT

Parameter Ref 14 Laboratory AQS (sediment lab)

Period Oct. 1 1977 -> Nov. 5 1978

A average 2.23 std. dev'n 0.33

B average 2.22 std. dev'n 0.27

Overall std. dev'n for data from different runs 0.30

Std. dev'n for data from the same run 0.27

Controllable contribution to overall std. dev'n 0.14

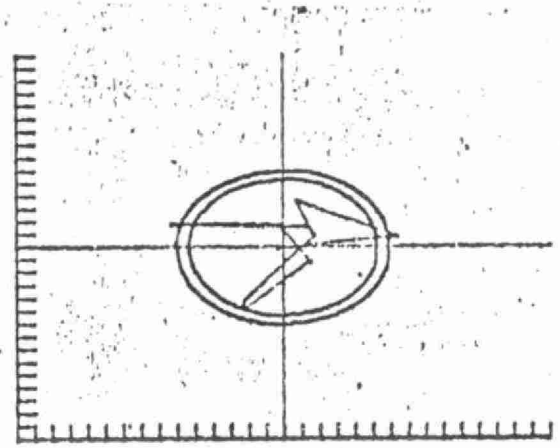
Inner circle = 2 x std. dev'n within-run data 0.53

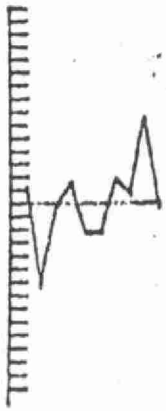
Outer circle = 2 x std. dev'n between run data 0.60

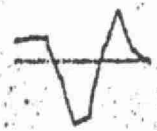
Concentration per division on the diagram .10

Calculated Warning limit for T and D 0.76

Calculated Control limit for T and D 1.13







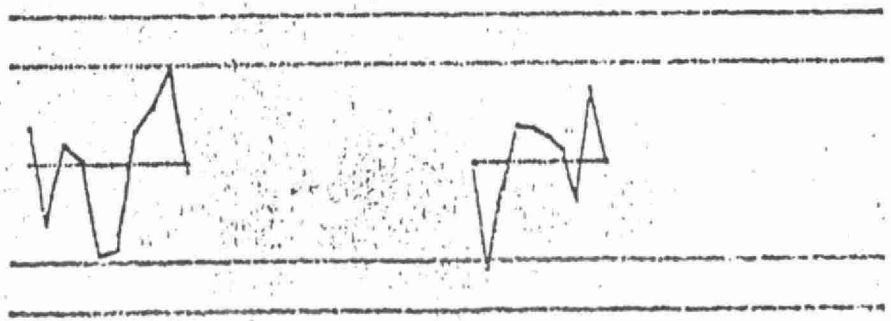
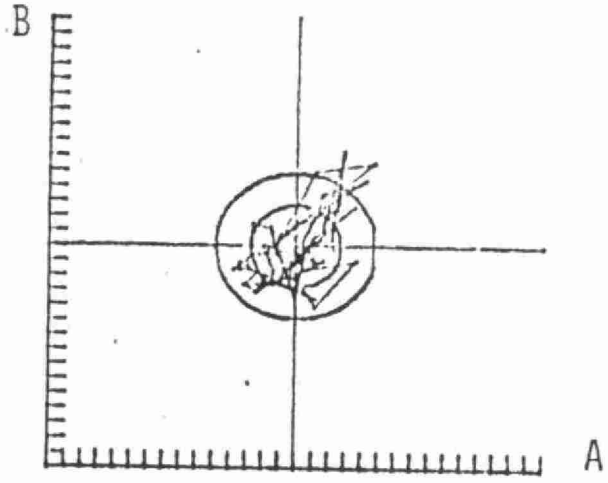
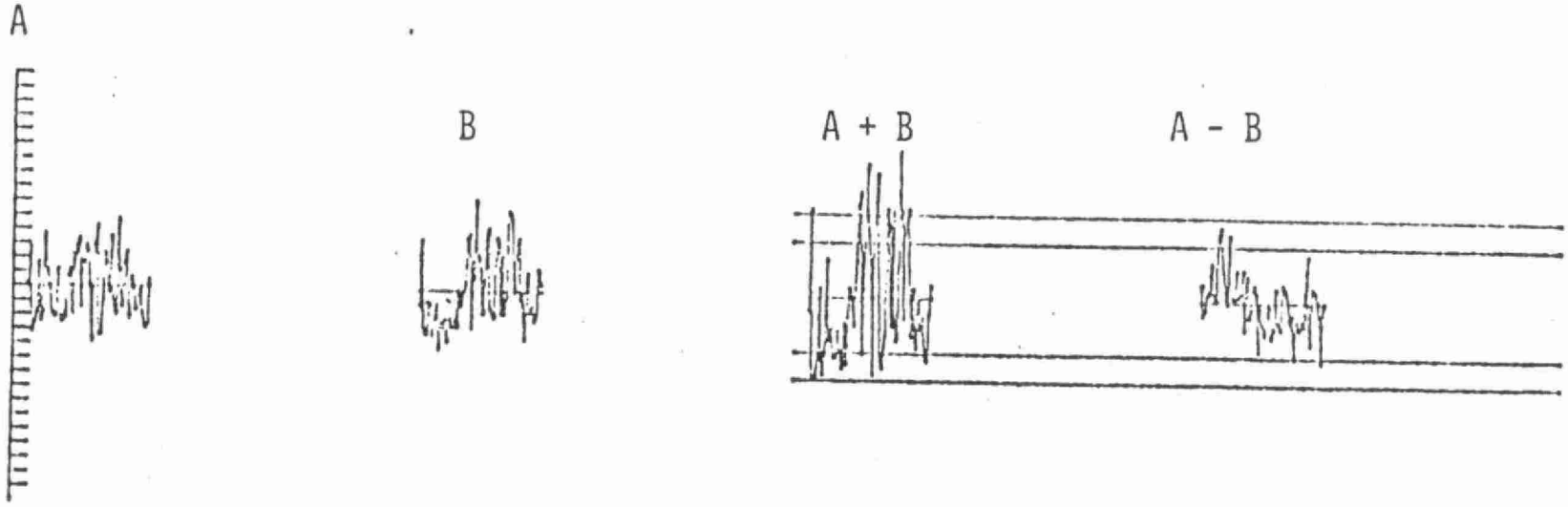


FIGURE V -

ARSENIC REFERENCE 15, 1976 & 1977 DATA (TO SEPT)





APPENDIX II

SELENIUM

AUTOMATED HYDRIDE METHOD

DIGESTION

ANALYSIS

RESIN SLURRY SYSTEM

FILTER SYSTEM

RESIN REGENERATION

AUTO-ANALYZER SYSTEM

CALIBRATION

INTERFERING ELEMENTS

PRECISION (ACETATE/SODIUM HYDROXIDE RESIN SLURRY)

THE DETERMINATION OF SELENIUM IN SEDIMENTS - AUTOMATED HYDRIDE METHOD

DIGESTION

1. Add 10 ml. concentrated nitric acid and 2 ml. concentrated sulphuric acid to 0.10 g., 0.20 g. or 0.50 g. dried, ground sample in a 250 ml. Erlenmeyer flask with ground glass neck. Place air condenser in neck.
2. Heat overnight (17 $\pm$ 1 hrs.) on hot plate set at 234°C. Position 4 setting on Thermolyne). No brown fumes should be present in air condenser following digestion and digestate and residue should be free of organic matter. Continue digestion and add more nitric acid if necessary.
3. Cool. Rinse condenser into flask with about 5 ml. distilled water.
4. Filter through fine filter paper (Schleicher and Schuell No. 589) into 50 ml. graduated Pyrex tube, rinse with distilled water and make up to 25 ml. mark.

HOT BLOCK PROCEDURE

1. Weigh 0.25 g into Technicon block digester tube. (60 ml)
2. Add 5 ml. 4:1 H_2SO_4/HNO_3.
3. Program to heat at 100°C for 30-45 minutes, then 250°C for 2.5 hours.
4. Filter and make up volume to 50 ml.

NOTE: The above procedure is used for the digestion of sediment samples for mercury.

ANALYSIS

1. Set up auto-analyzer and continuous filter as shown in Figures VI - VIII. Connect gas stream after phase separator to mid-point of open-ended heated quartz tube aligned along optical path of atomic absorption spectrophotometer (as for arsenic).

2. Install paper tape on filter cementing ends with Dvco cement to form continuous filter. Ensure guiding is optimum to prevent early tape breakage.

3. Set up the resin slurry recirculation system with regenerated Chelex 100 (200 to 400 mesh) suspended in malonic acid and ammonium hydroxide. Add 91.57 g. malonic acid (technical grade) to about 150 ml. concentrated ammonium hydroxide while stirring and continue to add ammonium hydroxide until the final pH is 6.00. Dilute to 200 ml. with distilled water. Mix in 85 ml. of wet regenerated resin and transfer to separatory funnel in recirculation system.

4. Ensure that the continuous filter and resin recovery systems are operating properly (discussed in more detail later).

5. Set up atomic absorption spectrophotometer. Conditions for the Varian AA-4 are as follows:

Adjust nitrogen gas flow for minimum noise and maximum sensitivity. Quartz tube heater control may also require adjustment.

6. Run high standard through the system initially to saturate absorption sites for selenium.

7. Set up standards, blanks, in-house references and sample digestates in Pyrex tubes in sampler. Run series of standards first and repeat until reproducible calibration curve is obtained, then follow with sample digestates. Place standards and blanks at intervals in sampler tray to check for change in sensitivity.

8. Continue as for Arsenic Determination.

RESIN SLURRY SYSTEM

A uniform suspension of resin can best be obtained by rapid circulation. Recirculate from the bottom of the 500 ml. separatory funnel back to the top through Tygon tubing using a high capacity peristaltic pump.
Change position of Tygon tube in pump rollers periodically to avoid rupture.

To shut down, close stopcock at bottom of separatory funnel prior to shutting off pump. Slurry is bled from recycle line through a short length of Teflon tubing attached to the appropriate flow tube in the Technicon pump.

FILTER SYSTEM*

The flow of filter feed of resin slurry plus diluted sample digestate should be in slight excess to that drawn through the filter to ensure the absence of air bubbles.

The flow of service (tap) water to the wash-off unit should be the minimum consistent with steady flow and

*Refer to Figures VII and VIII

efficient removal of resin from the paper tape. Removal of resin is aided by surface tension forces set up as air is also drawn down the resin drain-off tube if operated at the optimum flow rate.

The resin settling tank is designed to provide a sufficiently low flow rate that there is no resin carry-over to the drain line leading to the floor drain.

If there is no floor drain, a second tank and peristaltic pump can be used to discharge to a sink, but this is less satisfactory.

The resin can be recovered and regenerated periodically.

Algae growth in the resin settling tank may be a problem, but can be controlled by addition of a few drops of phenol at each shutdown of longer than one day.

RESIN REGENERATION

1. Pour off supernatant water in resin settling tank and transfer wet resin to a large beaker.
2. Add 2 bed volumes of 1 N HCl, stir and allow to settle. Decant off supernatant and add 5 bed volumes of distilled water in two or three treatments, decanting off the supernatant.
3. Maintain resin in moist state until ready to mix with malonate - ammonia buffer.

SELENIUM ANALYSIS

Instrument Operating Conditions

Varian AA-4

Wavelength	196.0 nm
Slit	300 nm
Current	AA-4 source 2mA
	EDL power source 8 watts
Mode	Absorbance
Damping	D (max.)
Scale	No expansion
Tube heater (Variac)	7.3 (140 V)
Exhaust vent	Close
Recorder Speed	20 cm/hr.
Recorder Sensitivity	2 mV span
	full scale deflection

TABLE IV

EFFECTS OF INTERFERING ELEMENTS ON SELENIUM DETERMINATION

Se in Soln (ppb)	ELEMENTS ADDED (ppm)	RECOVERY % NO RESIN TREATMENT	RECOVERY % RESIN IN MALONIC-NH_4OH
20	0.5 Cu, Co, Cd, Ni, Zn, Sn 5 Fe, Al	100	100
20	2.5 Co, Cd, Ni, Zn, Sn 3.0 Cu 3.5 Mn 5.0 Al 12.5 Fe	32	78
20	12.5 Cu, Co, Cd, Al, Ni, Zn Mn, Sn 246 Fe	19	47
40	1 Cu	53	100
40	2 Cu	28	97
40	5 Cu	15	93
40	10 Cu	11	92

NOTE: 20 & 40 ppb Se were used for calibration

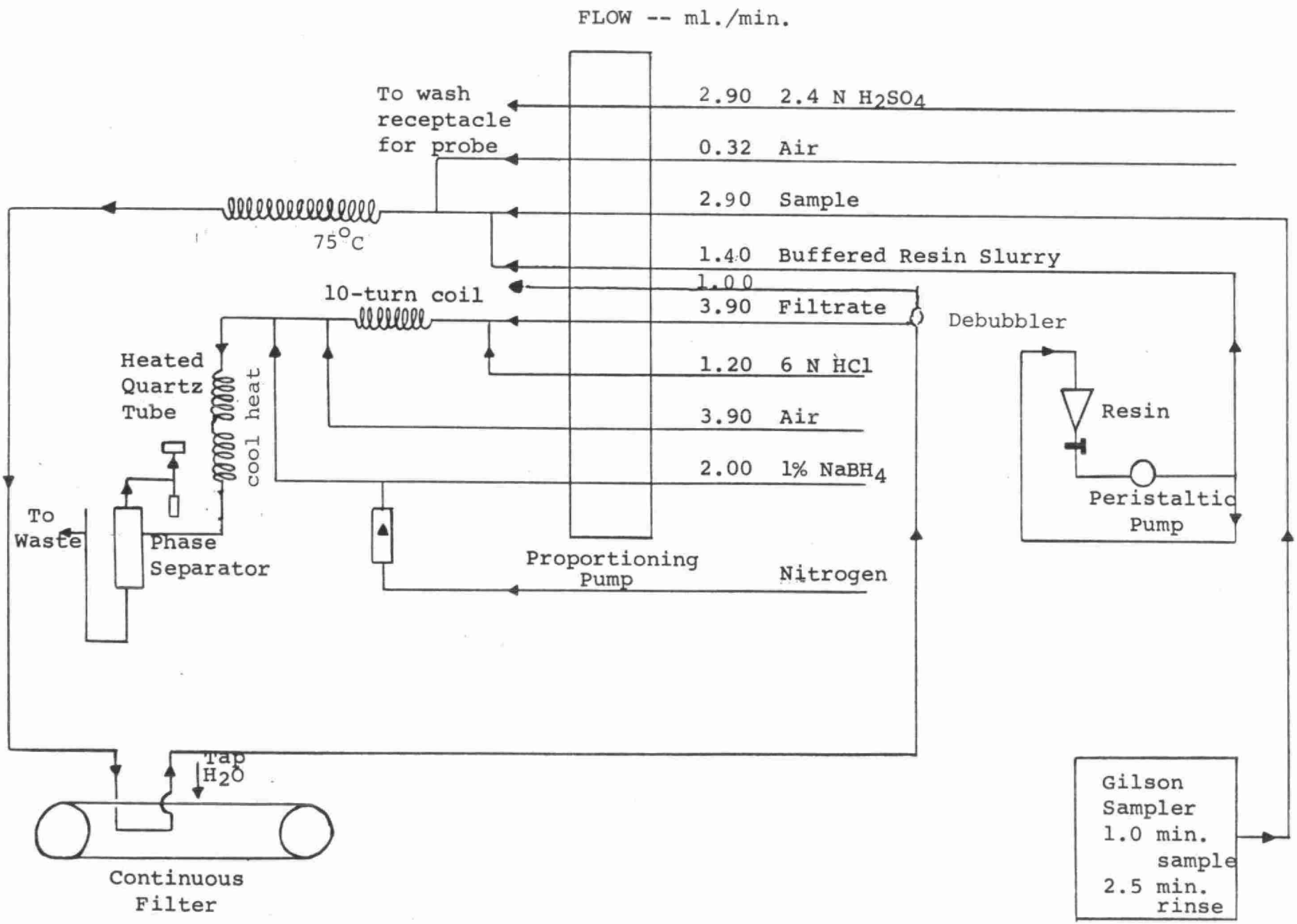


FIGURE VI - AUTOANALYZER SYSTEM FOR SELENIUM IN SEDIMENTS & SOILS

FIGURE VII - CONTINUOUS FILTER ASSEMBLY

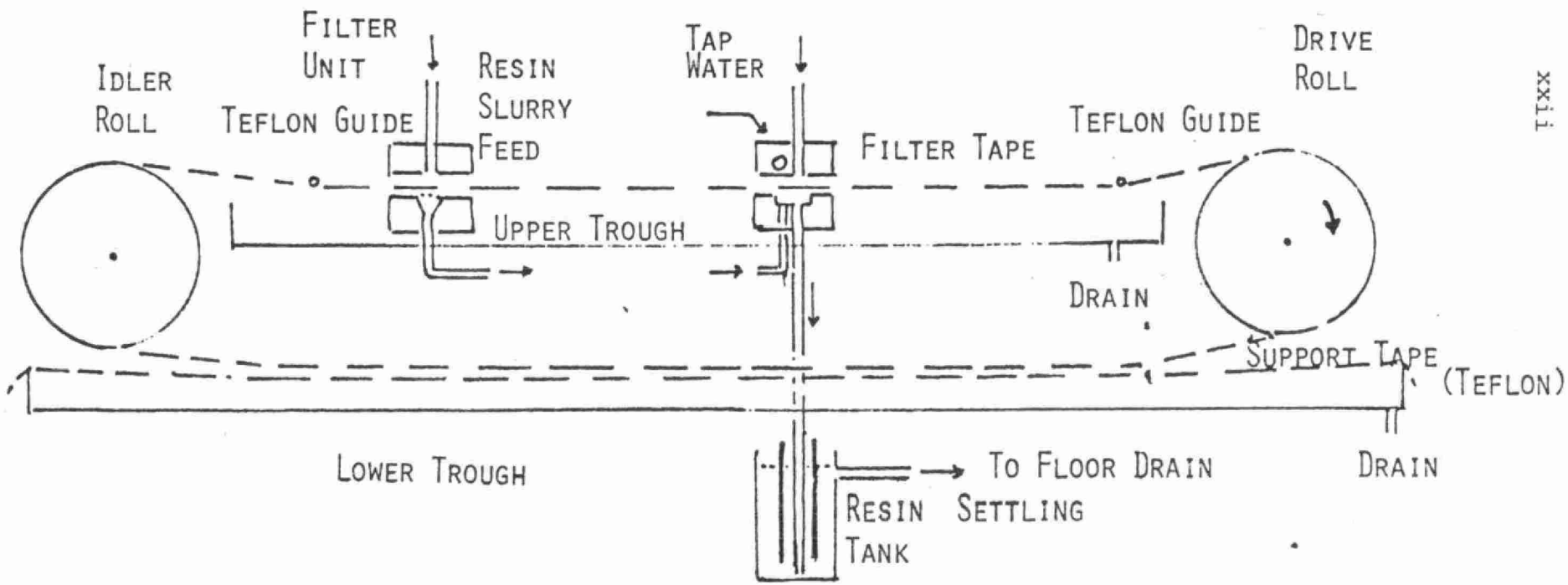
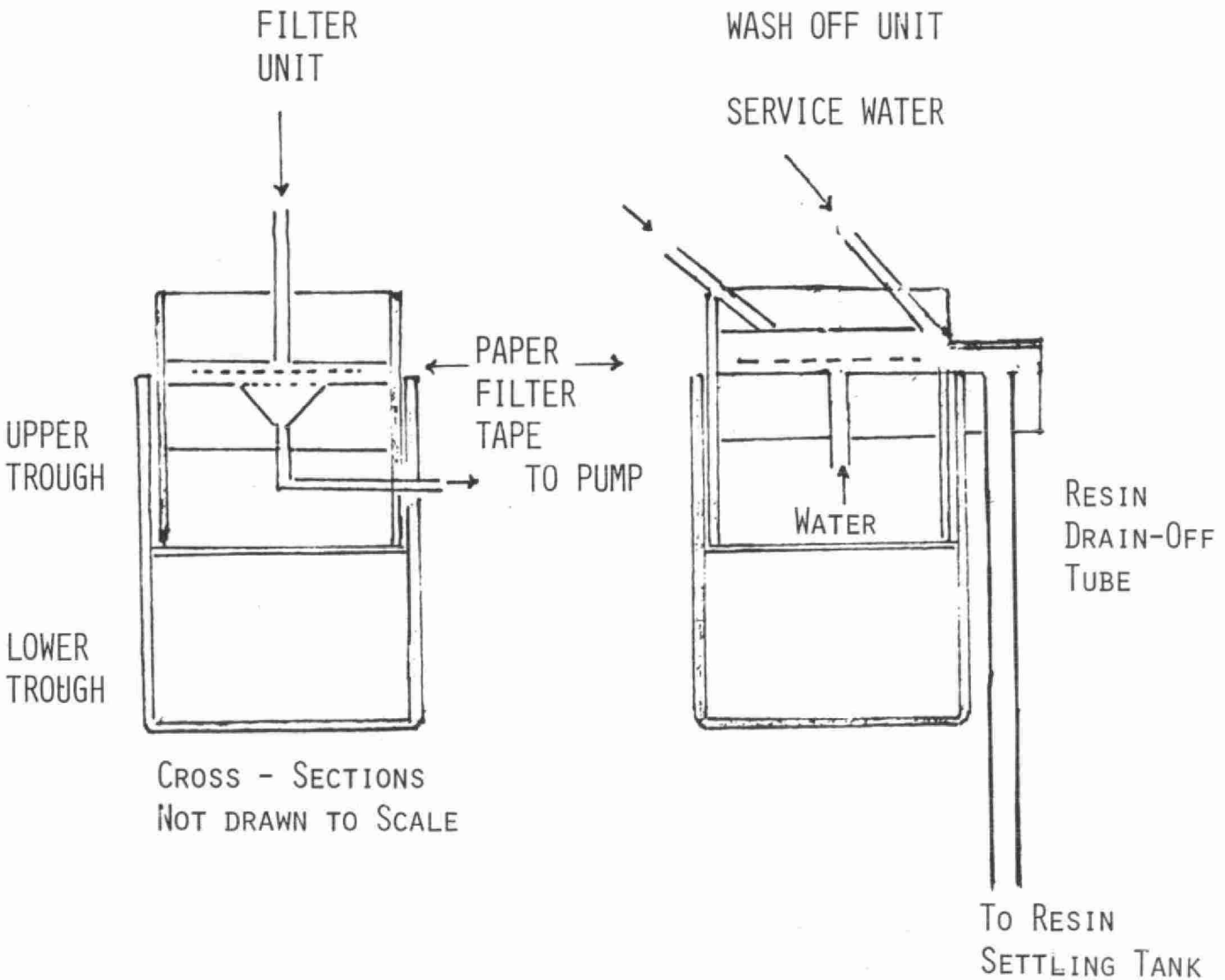


FIGURE VIII - CONTINUOUS FILTER ASSEMBLY



MATERIAL: Plexi-Glass

FIGURE - IX

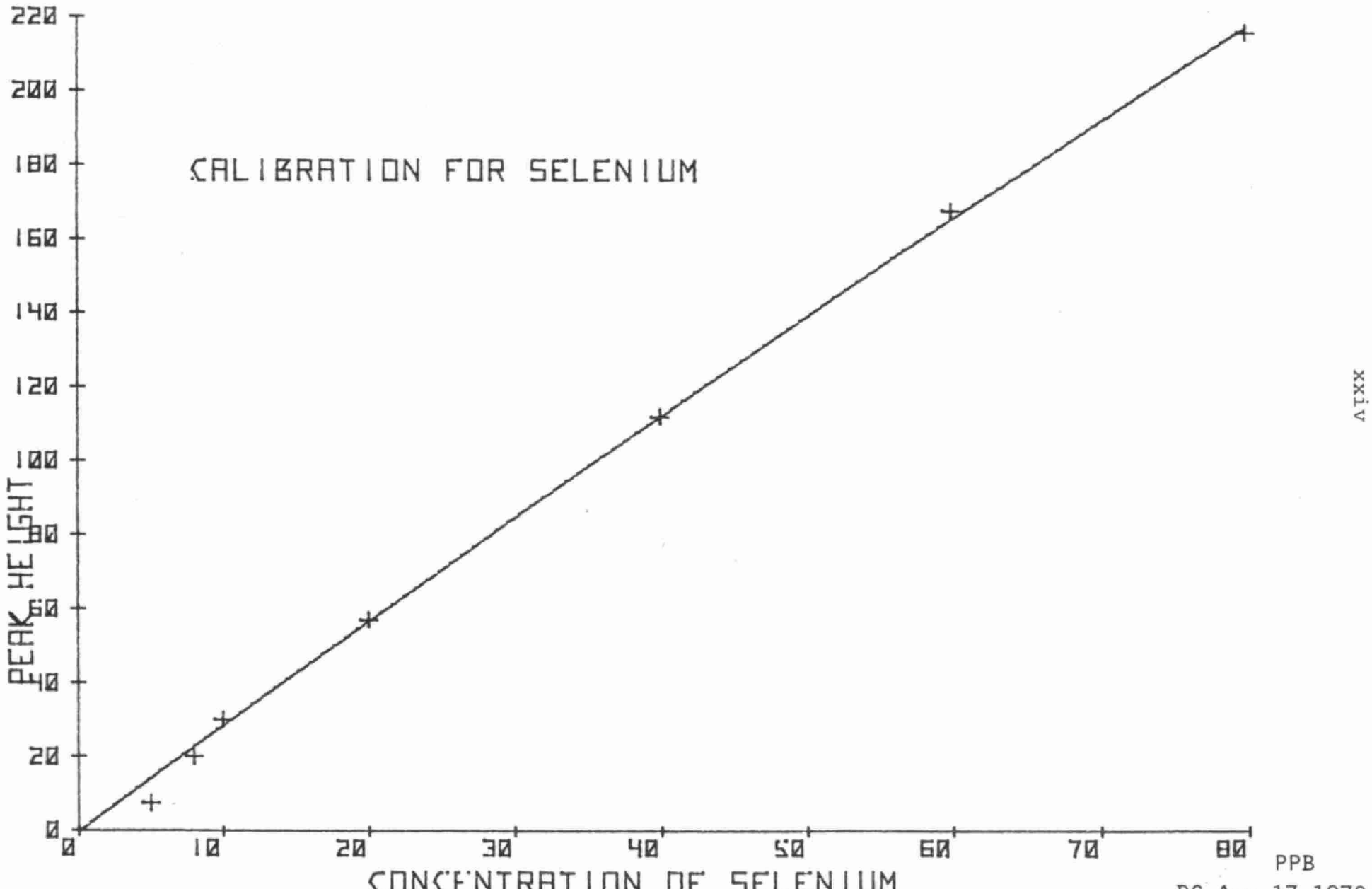

CALIBRATION FOR SELENIUM
PEAK HEIGHT
220
200
180
160
140
120
100
80
60
40
20
0
0
10
20
30
40
50
60
70
80
CONCENTRATION OF SELENIUM
PPB
DC Apr 17,1978

FIGURE X - SELENIUM WITH RESIN

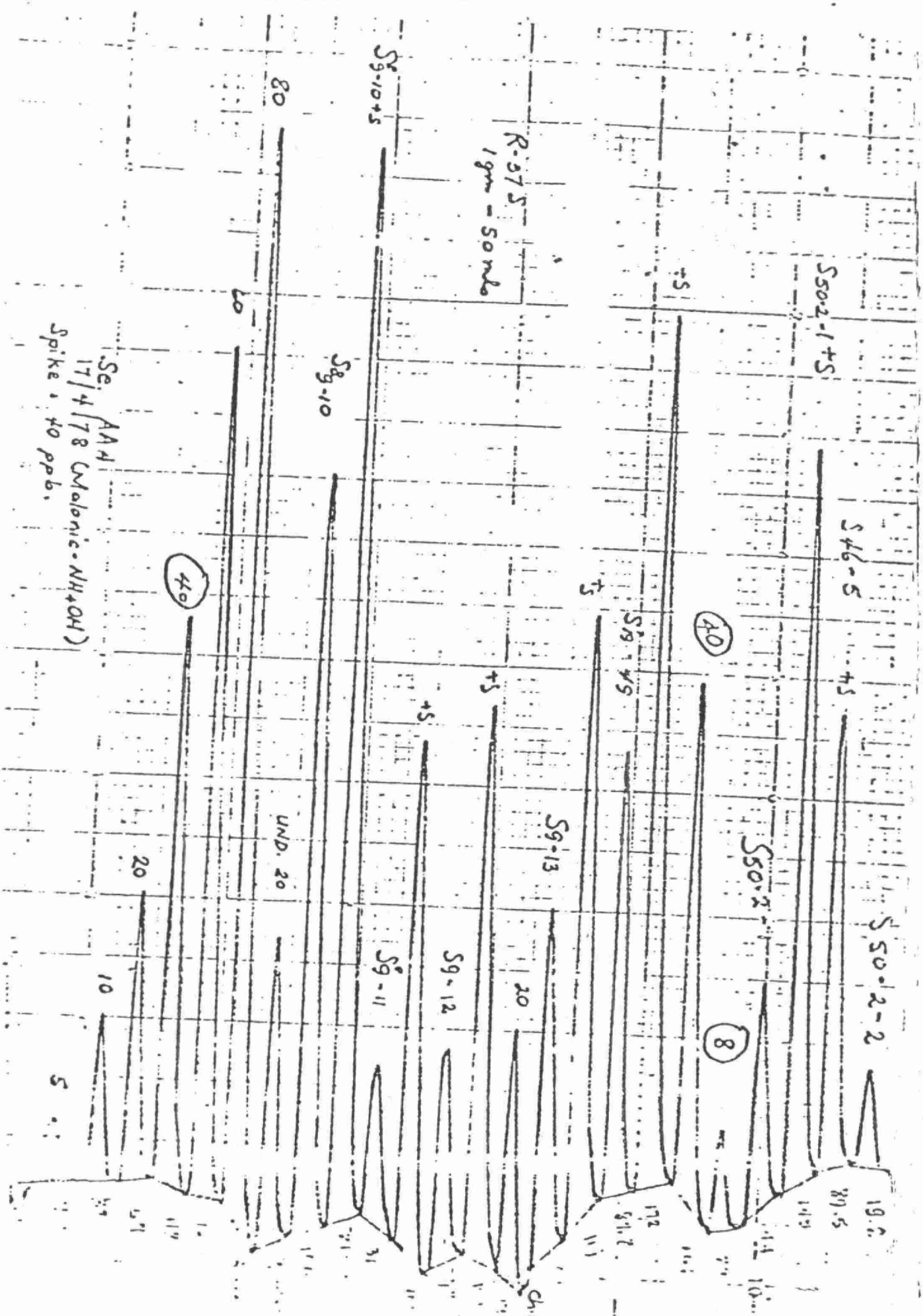


FIGURE XI - SELENIUM WITHOUT RESIN

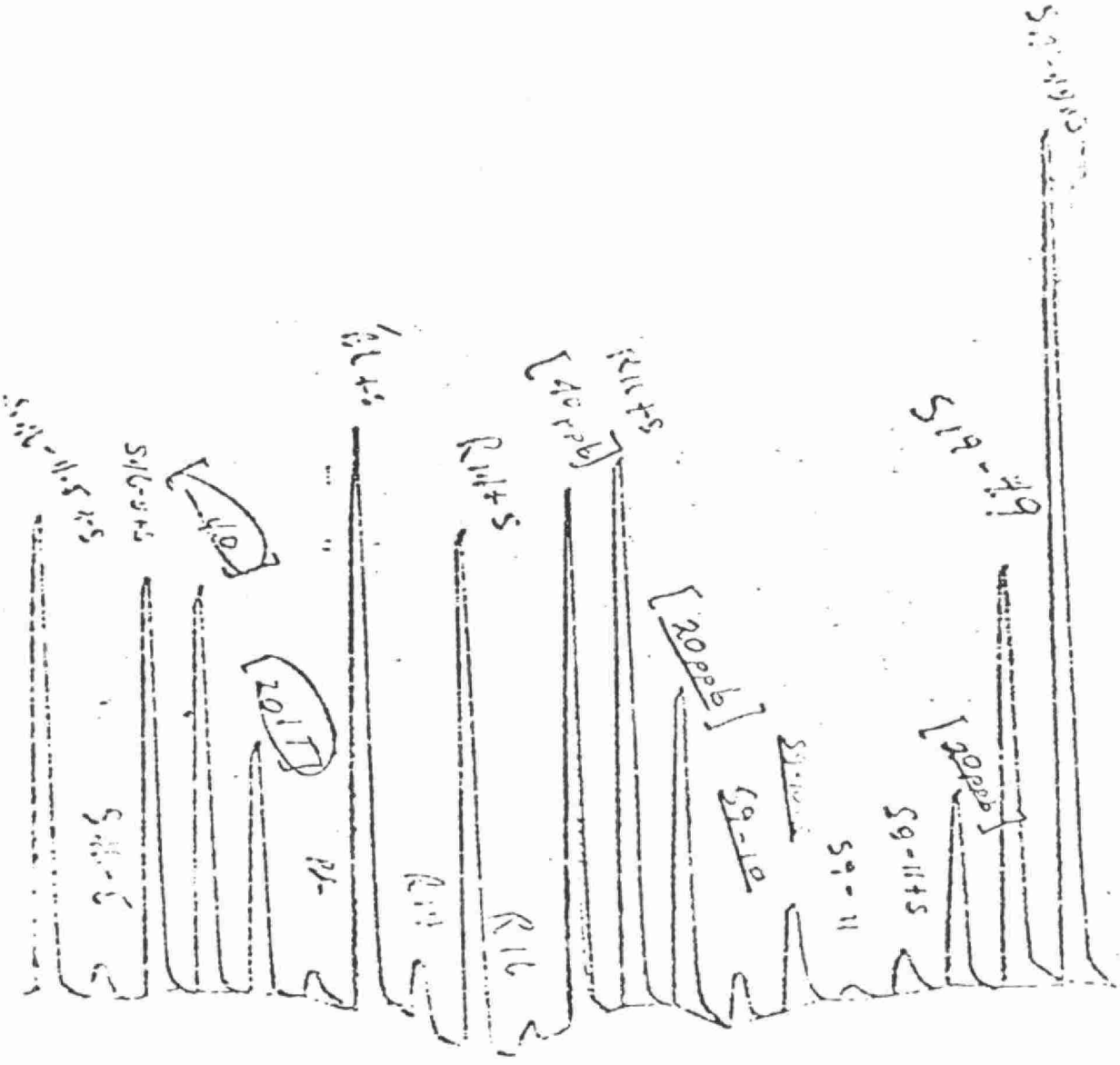


TABLE V

REPRODUCIBILITY OF SELENIUM ANALYSIS

Sodium acetate buffered resin slurry.
In-house Reference Samples analyzed at intervals June - September 1977.

Reference 14

Determination	ug/g Se
1	.21
2	.20
3	.22
4	.26
5	.19
6	.15
$\bar{X}$	.204

NOTE: $\bar{X}$ and RSD calculated from the 6 values listed above.
Interference suspected for Nos. 5 & 6.

Reference 7

Determination	ug/g Se
1	.23*
2	.37*
3	.37*
4	.40*
5	.49*
6	.64
7	.69
8	.61
9	.26*
10	.19*

*NOTE: Interference suspected.
Precision not yet determined for malonate/ammonia system.

TABLE VI

EFFECT OF DIGESTION CONDITON

ANALYSIS OF COAL FLY ASH

N.B.S. Standard Reference Material 1633

	ug/g
Certified Value*	9.4 ± 0.5

Hydride method: Chelex 100 - acetate buffer

Digestion condition		N.B.S. Fly Ash	Ref. 7
Sulphuric-nitric	1 g	10.3	1.44
	0.5 g	11.1	1.48
Perchloric-nitric	1 g	9.8	0.64
	0.5 g	8.5	xx
Hydrochloric-nitric			
	1 g	5.0	0.84
	0.5 g	6.0	xx

Analysis by:

*Isotope dilution spark source mass spectrometry and neutron activation.

xx None detected; suspected interference or volatilization loss.

Recoveries not determined with most recently used malonate buffer.